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Infrared and Raman spectroscopic investigations on ferroelectric lead hydrogen phosphate crystals

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Abstract : Lead hydrogen phosphate (LHP) or Lead monetite single crystals are grown by gel method Infrared and laser Raman spectra of ferroelectric $PbHPO_4$ have been measured at room temperature in the frequency regions 4000 — 200 cm^{-1} and 4000 — 10 cm^{-1} respectively. Vibrational band assignments have been made, which are consistent with the C_s point group symmetry of the ferroelectric phase The assignments made for this ferroelectric crystals are classified into three parts viz. (i) lattice modes, (ii) PO_4 internal modes and (iii) High frequency H-modes

Keywords : Infrared spectra, Raman spectra, vibrational band assignments

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1. Introduction

From the structural stand point $PbHPO_4$ (LHP) crystal is most conformable to the quasi one-dimensional hydrogen bonded ferroelectric. Carvalho and Salimas [1] applied their quasi one-dimensional Ising model to the ferroelectric properties of $PbHPO_4$. This crystal has the same crystal space group P_c or C_S^2 at temperature above and below the transition temperature (T_c = 310K). A neutron diffraction study of LHP at room temperature reported by Negran *et al* [2] yielded particularly single crystal structure with monoclinic symmetry with two formula units per cell. As shown in Figure 1, the PO_4 groups are linked into chains along c-axis by short O-H--O bonds; but these chains are not cross-linked to one another as in potassium dihydrogen orthophosphate (KDP). The O-H--O hydrogen bonds play an important role in the transition from ferroelectric to paraelectric mechanism at the T_c.

The infrared and Raman spectra of powdered samples were first reported by Blinc *et al* [3] and proposed a pseudo spin tunnelling model for the phase transition of LHP in analogy to the similar theory for KDP in interpreting their results. A complete vibrational band assignments studies for the powdered LHP crystals comparing both infrared and laser Raman spectra at room temperature have been reported in the present work. The O-H--O hydrogen bonds in $PbHPO_4$ are found to be similar to those in $PbHAsO_4$ KH_2PO_4 and KH_2AsO_4. LHP

crystal is monoclinic at room temperature [2]. The PO_4 groups are linked by O-H--O bonds to form a system of linear chains along C-axis. The O-H--O distances are 2.52 Å [2]. Hydrogen positions are 0.22 Å from the pseudo-centre of symmetry in O-H--O bonds, so that O-H bond length is 1.04 Å. The hydrogen bonds should be thus close to those in KH_2PO_4.

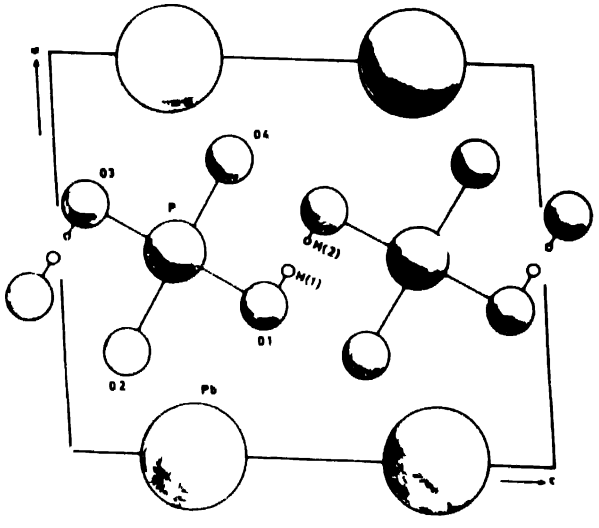

Figure 1. The crystal structure of $PbHPO_4$ projected on the a c plane

In $PbHPO_4$ however a system of linear O-H--O chains is dealt with, rather than a layer like hydrogen bond network in which only half of the oxygens are hydrogen bonded as in KH_2PO_4 [4] $PbHPO_4$ is not isomorphous with orthorhombic $BaHPO_4$ crystals and triclinic $CaHPO_4$ crystals. Preliminary results from a structural study have shown that the ferroelectric phase of deuterated isomorph LDP has the same space group as LHP (Negran *et al* [2]). The space group of the para-electric phase of the LDP is taken to be $P_2/c|C_{2h}^4|$ (Negran *et al* [2]), as was thought previously to be the case of LHP. However, in view of the recent work on LHP (Lockwood *et al* [5], Nelmes *et al* [6]) this assumption must be treated with caution.

2. Experimental

Based on the principle that good quality crystals can be grown in the gel medium, the gel technique of growing $PbHPO_4$ has been adopted in the present work. The BDH Analar chemicals and double distilled water have been used here. Growing of larger LHP crystals is very difficult because of low solubility of this compound. In the present method, one of the reactants, orthophosphoric acid (0.5M-1. 5M) was incorporated with the gelling mixture of density varying between 1.02-1.09 gm-cm^{-3} for the pH range 2-10, followed by the slow diffusion of another reactant supernatant lead nitrate solution (0.5M-2M). The crystals grown in higher density and higher pH value gels are found to be opaque. Good transparent crystals are well grown in the lower density gels 1.03-1.04 gm-cm^{-3} with low pH values 2-3.

The Fourier transform infrared and far infrared spectra of this crystal have been measured respectively on Perkin Elmer-1760 and 983 spectrometers in the regions 4000-500 cm^{-1} and 1000-200 cm^{-1}. The laser Raman spectra have been observed in the region 4000-10 cm^{-1}; on DILOR Z24 Raman spectrometer using 514.53 nm radiation from an Argon ion laser (100 mW) for excitation. The spectra are presented in Figures 2 to 4 and the observed frequencies with thier assignments are summarized in Table 1. The frequencies for all sharp bands are expected to be accurate to ± 1 cm^{-1}. All spectra are recorded at 303° K.

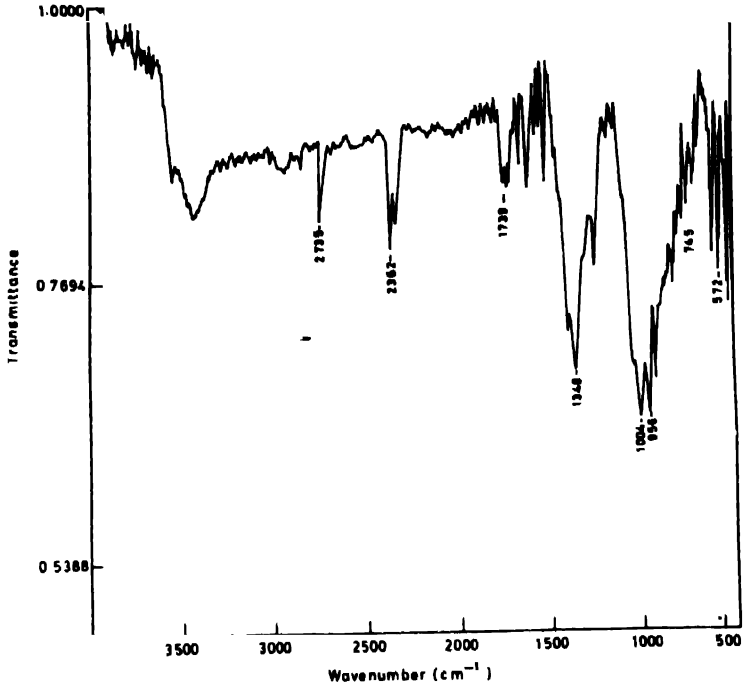

Figure 2. Fourier transform infrared spectrum of lead hydrogen phosphate.

3. Results and discussion

Vibrational band assignments :

Figure 1 shows the crystal structure of the ferroelectric phase of lead hydrogen phosphate in a projection of the unit cell on the ac plane. The H atoms disordered over two sites related by a centre of inversion at the mid point of the O-H--O bonds. The PO_4 groups are linked by the hydrogen bonds to form chains along the C-axis. These chains are well-separated from each other by the lead atoms in the a-axis. As far as lead hydrogen phosphate [7] we may consider the PO_4^{3-} to be molecular entities so that the number of modes may be subdivided into PO_4

internal modes, external or lattice modes and high frequency H-modes. The internal modes should occur at higher frequencies than the lattice modes. The high frequency modes of

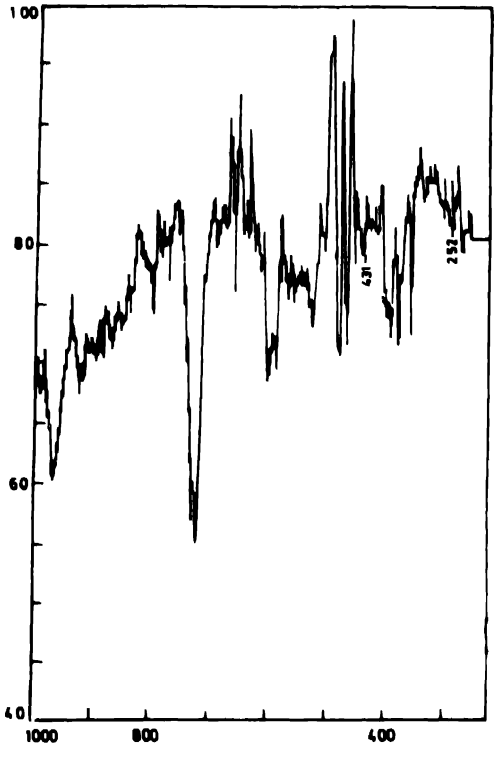

Figure 3. Far-infrared spectrum of lead hydrogen phosphate in the range of 1000 - 200 cm $^{-1}$

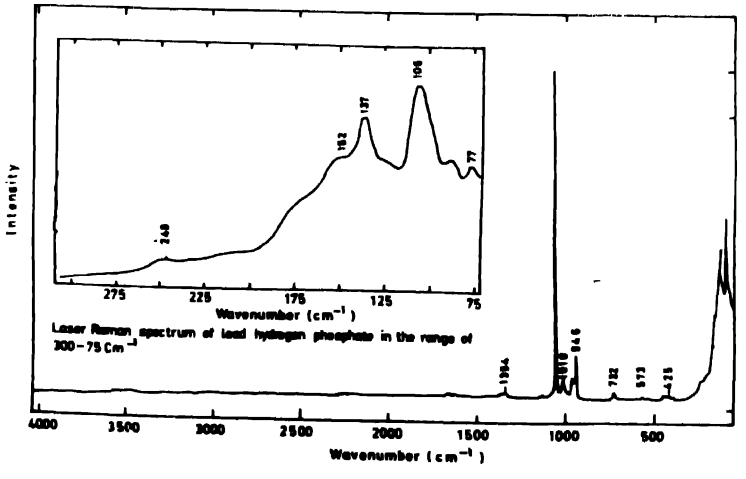

Figure 4. Laser Raman spectrum of lead hydrogen phosphate in the range of 4000 - 10 cm^{-1}

protons involved in the O-H--O bonds are expected to appear at frequencies beyond 1200 cm^{-1}. We now discuss the results obtained in the different spectral regions; the lattice phonon region, the PO_4 internal vibration region and the high frequency H mode region.

Table I. Vibrational spectra and band assignments of lead hydrogen phosphate.

Raman Frequency cm^{-1} * Intensity	Infrared Frequency cm^{-1} * Intensity	Description
77 (MS)	---	$\nu_{O....O}$ (HPO_4) libration modes and polar lattice mode
106 (VS)	—	
137 (S)	---	
152 (M)	---	
249 (VW)	252 (W)	
425 (VW)	431 (W)	ν_2 (PO_4)
573 (VW)	572 (MS)	ν_4 (PO_4)
732 (VW)	745 (M)	δ (OH)
946 (M)	956 (VS)	ν_1 (PO_4)
1018 (W)	1004 (VS)	ν_3 (PO_4)
1354 (VW)	1348 (S)	δ (OH)
	1739 (MS)	ν(OH) + combinations and overtones
	2362 (M)	
	2735 (M)	

* VS - Very strong; S - Strong : M - medium:
MS - medium strong : W - Weak; VW - Very weak

3.1 Lattice vibrations :

Lattice vibrations which involve the motions of lead atoms and the PO_4 complexes as a whole appear in the far infrared region. Further, a soft mode is expected below 110 cm^{-1} [8]. The peak around 250 cm^{-1} may represent probably the O-O hydrogen bond stretching vibration involving liberation motion of the HPO_4 group. Such O-O stretching mode could occur as well around 250 cm^{-1} in $CaHPO_4$ and around 155 cm^{-1} to 145 cm^{-1} $BaHPO_4$ [9]. In the present work, these bands appear in the characteristic region.

3.2 PO_4 Internal vibrations :

In this region, we expect to find the internal vibrations of the PO_4 tetrahedra and the out or in plane O-H deformation vibrations. If there would be a short symmetric O-H--O bond we should as well find the O-H stretching frequency in this region. The free PO_4 ion represents a regular tetrahedron of point group T_d and has four distinct vibrational frequencies. In order of increasing frequency these modes are a Raman active doubly degenerate vibration ν_2 (E), a triply degenerate Raman and infrared active vibration ν_4 (F_2), a Raman active totally symmetric vibration ν_1 (A_1) and a triply degenerate Raman and infrared active vibration ν_3 (F_2). In aqueous solution the PO_4^{3-} frequencies [10] are ν_2 (E) = 425 cm^{-1}, ν_4 (F_2) = 573 cm^{-1}, ν_1 (A_1) = 946 cm^{-1} and ν_3 (F_2) = 1018 cm^{-1}.

The stretching ν_3 (F_2) band in $PbHPO_4$ is centred at around 1020 cm^{-1} and does not appear to be split. The protons thus seem to have a relatively small influence on the distortion of the PO_4 group on the low frequency side of the band. There are two weak shoulders at 946 cm^{-1} and 732 cm^{-1} which may represent the weakly allowed ν_1 (A_1) band and the O-H deformation respectively. The strong and sharp ν_4 (F_2) band at 573 cm^{-1} is as well not split. The same is true for the weaker ν_2 (E) band at 425 cm^{-1}.

The O-H vibrations are usually rather weak in Raman spectrum as compared to PO_4 internal vibrations and lattice vibrations. A comparison of the infrared and Raman spectra thus allows an additional check on the correctness of the assignments of characteristic group frequencies. No strong Raman scattering was found above 1200 cm^{-1}. This confirms the present assignment that only O-H vibrations give rise to infrared absorption in this region. The strong Raman lines at 1018, 946, 573 to 500 and 425 cm^{-1} obviously represent the ν_3 (PO_4), ν_1 (PO_4), ν_4 (PO_4) and ν_2 (PO_4) normal vibrations thus again confirming the assignment of the infrared absorption bands.

3.3 High frequency H mode :

The infrared spectra of $PbHPO_4$ is very close to the one observed [11] in KH_2PO_4. It shows the so called A, B, C band structure [$PbHPO_4$: ν_A = 2750 cm^{-1}, ν_B = 2350 cm^{-1}, ν_C = 1250 cm^{-1}] which is characteristics [11] for medium strong O-H--O bonds. The main cause of absorption in the rather broad spectral range between 2880 and 1600 cm^{-1} is the O-H stretching vibration. The A, B, C peaks are presumably caused by Fermi resonance and combinations with the in plane (δ O-H) and out of plane (ν O-H) deformations. The peak around 1350 cm^{-1} is due to the in plane O-H deformation vibration. The above data definitely rule out the possibility of a symmetric H bond in $PbHPO_4$. The infrared spectra suggest an off-centre location of the hydrogen.

4. Conclusions

A complete vibrational assignment has been made available for ferroelectric phase lead hydrogen phosphate crystal using Fourier Transform infrared and laser Raman spectra in the present investigation. The results obtained in the different spectral regions *viz*; lattice phonon region, PO_4 internal vibration region and the high frequency H mode region have been discussed. A comparison of the infrared and Raman bands made available in the present work confirms the correctness of the vibrational assignment for lead hydrogen phosphate.

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